

The phase diagramm of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ revisited

M. Paraskevopoulos¹, J. Hemberger¹, A. Loidl¹, A. A. Mukhin², V. Yu. Ivanov² and A. M. Balbashov³

¹*Experimentalphysik V, Elektronische Korrelationen und Magnetismus,
Institut für Physik, Universität Augsburg, D - 86159
Augsburg, Germany*

²*General Physics Institute of the Russian Acad. Sci.
117942 Moscow, Russia*

³*Moscow Power Engineering Institute, 105835 Moscow, Russia
(submitted to PRL Oct.98)*

We report on detailed susceptibility and magnetization studies in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x \leq 0.2$. We arrive at a phase diagram which shows a ferromagnetic ground state for $0.1 \leq x \leq 0.15$ followed by a canted antiferromagnetic phase at higher temperatures, not in agreement with present canonical conjectures. The phase diagram indicates the importance of structural aspects and superexchange interactions for the magnetic phases at low Sr concentrations.

It is now half a century ago that Jonker and van Santen [1] demonstrated that the manganite perovskites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, in which the trivalent La ion is substituted by a divalent cation, reveal many interesting and puzzling phenomena. On substitution with A^{2+} , the antiferromagnetic (AFM) ground state of stoichiometric $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-}$ becomes ferromagnetic (FM) for $x \geq 0.2$ [1,2]. At that time the FM properties of $(\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{2-})_{1-x}(\text{A}^{2+}\text{Mn}^{4+}\text{O}_3^{2-})_x$ were explained by a strong positive $\text{Mn}^{3+}\text{-Mn}^{4+}$ exchange interaction [1]. In a famous theoretical work it was de Gennes [3] to establish the close connection of electrical transport and magnetic properties via an interplay of Mn-O-Mn superexchange (SE) interactions with Zener's double exchange (DE) [4]. Driven by an increasing concentration of mobile holes, the insulating (I) and AFM structure passes via a canted AFM (CA) structure to a purely metallic (M) and FM ground state [3]. Recently an overwhelming interest in these compounds arose due to the observation of a negative colossal magnetoresistance (CMR) in a certain composition range [5]. These CMR effects at the FM phase transition were explained within extended double exchange models [6] taking also Jahn-Teller distortions into account [7].

An early structural phase diagram has been presented by Bogush *et al.* [8]. They showed that on decreasing temperature pure LaMnO_3 reveals the sequence rhomboedral (R) to orthorhombic (O) and finally to another orthorhombic structure (O'). In the O phase the three octahedral Mn-O bond lengths are almost equal, while in the O' phase, due to a long-range Jahn-Teller (JT) distortion, these bond lengths become strongly anisotropic. On increasing hole doping, and concomitantly with an increasing concentration of Mn^{4+} , the Jahn-Teller distortions become suppressed and for $0.15 < x < 0.2$, the undistorted O phase extends to the lowest temperatures. An electronic phase diagramm for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \leq 0.5$) has been published by Urushibara *et al.* [9].

That the $x-T$ phase diagram in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for low doping concentrations ($x < 0.2$) is even more complex, has been established by Kawano *et al.* [10], Yamada *et al.* [11] and Zhou *et al.* [12]. In these phase diagrams it has been explicitly assumed that the regime where the resistivity decreases with decreasing temperature ($\frac{d\rho}{dT} > 0$) is metallic and reveals a simple ferromagnetic spin arrangement and that the low temperature insulating ground state ($\frac{d\rho}{dT} < 0$) exhibits a CA structure for $x < 0.15$. Based on systematic heat capacity, magnetic susceptibility, magnetization and magnetoresistance experiments on single-crystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with concentrations $0 \leq x \leq 0.2$ we will show that these phase diagrams are not correct. Our results reveal that in this doping regime the Jahn-Teller distortions play a more fundamental role than the ferromagnetic double-exchange interactions.

Single crystals of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, with concentrations $0 \leq x \leq 0.2$ were grown by the floating zone method with radiation heating in air atmosphere. X-ray diffraction of crushed single crystals revealed high-quality single-phase materials. However X-ray topography indicated twinned crystals. An over-all phase diagram for $x < 0.5$ and $T < 1000$ K has been published recently [13]. To establish a detailed and complete phase diagram, the magnetic susceptibility and magnetization was measured using an ac susceptometer in fields up to 16 T and for temperatures $1.5 \text{ K} < T < 300 \text{ K}$ and a dc SQUID magnetometer for fields up to 7 T and for temperatures $1.5 \text{ K} < T < 300 \text{ K}$.

In Fig.1 the magnetic ac-susceptibility of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is plotted versus temperature for various doping levels. In the low doping regime (inset of Fig. 1), a pronounced peak at about 125 K -140 K indicates the paramagnetic (PM) to CA transition. The transition temperature T_{CA} significantly shifts towards low temperatures as the Sr concentration is increased. A second anomaly at about 180 K probably indicates a further structural anomaly. For the samples with $x = 0.1$ and $x = 0.125$, one can identify three transitions as the temperature is lowered. For this concentrations

a small anomaly, which indicates a structural transition, precedes the low-temperature magnetic transition ($x = 0.1$: $T_{CA} = 150$ K, $T_{O \rightarrow O'} = 115$ K, $T_C = 105$ K; $x = 0.125$: $T_{CA} = 180$ K, $T_{O \rightarrow O'} = 155$ K, $T_C = 140$ K). For $x = 0.15$ this sequence of structural and magnetic transitions appears in a narrow temperature range. It will be the aim of this paper to provide experimental evidence for the nature of this magnetic and structural transitions. For $x = 0.175$ we detected a strong increase of χ_{ac} at $T_C = 285$ K followed by a significant decrease on passing the rhomboedral to orthorhombic phase transition at $T_{RO} = 185$ K. From the plot of the inverse susceptibility we denoted one further phase transition at higher temperatures ($x = 0.1$: $T_{OO'} = 310$ K; $x = 0.125$: $T_{OO'} = 270$ K). These transitions are also clearly indicated by a significant increase of the resistivity on passing from $O \rightarrow O'$ [13]. At this point we clearly want to state that a interpretation of the structural anomalies was only possible taking the published neutron scattering results into account [10,11,14,15]

In the next step we investigated the magnetic ground state of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Fig. 2 shows the magnetization at 10 K for various compositions ($x \leq 0.2$) as a function of the magnetic field. Fig. 2 demonstrates that the samples with $x < 0.1$ are in a CA phase, which we conclude from the fact that there exists a spontaneous magnetization M_S which is followed from a linear increase of the magnetization M as the magnetic field is further raised. It is remarkable that there is no sign of saturation even at an applied field of 14 T. This behavior corresponds to the predictions of de Gennes [3] for the manganites in the canted phase. The basic effect is that the external magnetic field enforces a continuous reduction of the canting angle. In addition, the initial value of the spontaneous FM magnetization increases with x , a fact that directly demonstrates the reduction of the canting angle on hole doping. The inset a) of Fig. 2 shows FM hysteresis loops for this doping regime. Both the remanent magnetization and the remanent field increase on increasing hole doping. For higher doping rates ($x \geq 0.1$) we find the typical characteristics of an FM state with the magnetization reaching saturation within 2 T. There is a complete parallel alignment of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ spins as can be seen from the value of the saturated magnetization which approaches the classical spin-only value of $3.9 \mu_B / \text{Mn ion}$ (inset b) of Fig. 2). We would like to state that for concentrations $0.1 \leq x \leq 0.2$ the FM saturation looks very similar within the experimental uncertainties. Of course, we can not exclude a small canting angle ($\theta \lesssim 10^\circ$) but there is definitely a significant change in the magnetic ground state between $x = 0.075$ and $x = 0.1$. For all further discussions we assume a weak ferromagnetic ground state (large canting angles) for $x \leq 0.075$ and strong ferromagnetism (low or zero canting angle) for $x \geq 0.1$.

In the following we concentrate on the sample $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, although the same conclusions can also be drawn for $x = 0.125$. In order to understand the evolution of the different magnetic states as a function of temperature and magnetic field, we have measured the magnetization up to 14 T at various temperatures. Fig. 3 shows some representative results. For $T > T_{CA} = 150$ K the magnetization curves reveal the signature of a typical paramagnet. As the temperature is lowered below T_{CA} , we observe the evolution of a spontaneous magnetization M_S , which grows upon further cooling. As the external magnetic field is raised there is at first no obvious sign of saturation. The magnetization seems to behave like a canted AFM. At a given value of the applied field, characteristic for each temperature, jumps in the magnetization occur inducing a higher magnetization. The first loop at lower field signals a field-induced structural transition [16], from the JT-ordered phase O' to the orthorhombic phase O , accompanied by a step-like reduction of the canting angle which yields a higher magnetization. At the subsequent second hysteresis loop the sample undergoes a further transition into a FM state reaching the full magnetization. With decreasing temperature this anomalies are shifted to lower temperatures and finally disappear below $T_C = 105$ K.

Similar observations, as those presented in Fig. 3 have also been derived for crystals with a Sr concentration $x = 0.125$, although in this case the two subsequent hysteresis loops are not so nicely separated and it seems that the structural and magnetic phase transitions are closer coupled in temperature. Finally, for $x = 0.15$ we were not able to detect any hysteresis loops, neither in magnetization nor in magnetoresistance measurements. However, it seems clear that ferromagnetism is established below $T_C \simeq 200$ K, while for temperatures $200 \text{ K} < T < 240 \text{ K}$ the magnetization is not saturated in fields up to 14 T. But the $M(H)$ curves for magnetic fields $H > 0.5$ T always reveal a continuous curvature and never show a constant slope as observed for $x = 0.1$ at $T = 145$ K, characteristic for a canted structure. We are not able to detect clear indications of field induced structural phase transitions. It is possible that in this concentration regime all transitions appear in a narrow temperature range but we favour an explanation in terms of a phase separation.

Based upon these experimental results we tried to construct a structural, magnetic and electronic phase diagram which is compatible with the published experimental results. The phase diagram is simple at low strontium concentrations ($x < 0.1$). The transition into the CA ground state is clearly documented in the inset of Fig. 1 and in Fig. 2. As shown in the inset of Fig. 1, there exist slight anomalies in the susceptibility just below 200 K. It is unclear if they signal some kind of structural phase transition. Recently, a significant anomaly in the temperature dependence of the orbital order parameter has been observed in pure LaMnO_3 just above T_N [17]. In this system, driven by the long-range JT distortion orbital order is established at 800 K.

The phase diagram becomes much more complicated at higher concentrations. Our results provide clear experimental evidence that for $0.1 \leq x \leq 0.15$ the ground state is, within experimental accuracy, ferromagnetic and is followed for $x = 0.1$ and $x = 0.125$ by a canted spin state at elevated temperatures. And indeed, using neutron diffraction techniques, Argyiou *et al.* [14] have observed the temperature dependence of the canting angle Θ for $x = 0.125$ and observed a continuous decrease between 220 K to 160 K and a lock-in like phenomenon of the canting angle at approximately 20° close to 160 K, in close agreement with our experimental results. A very weak but finite AFM Bragg reflection has also been reported by Kawano *et al.* [10] for the same Sr concentration which again indicates an almost vanishing canting angle.

This observation of the sequence PM \rightarrow CA \rightarrow FM is in clear contradiction to all experimental phase diagrams published so far and of course calls for a different physical interpretation of the coupling of electronic and magnetic phenomena. It is clear now that the sequence metallic ($\frac{d\rho}{dT} > 0$) \rightarrow insulating ($\frac{d\rho}{dT} < 0$) can not be explained within a simple double-exchange picture which rests upon the sequence FM \rightarrow CA. We see no possibility to explain these results by an electronic phase separation as has been proposed theoretically [18] and has been observed experimentally in the Ca doped system [19]. In pure AFM clusters the hysteresis loops would shift to higher fields as the temperature is lowered, opposite to what is observed experimentally (see Fig. 3).

For a correct interpretation of our results it is necessary to take into account the results of recent neutron diffraction investigations [10,15] which reveal that close to $x = 0.125$ the pseudocubic high-temperature orthorhombic phase O, is followed by the JT distorted O' phase and finally transforms again into a pseudocubic O'' phase which reveals superstructure reflections due to charge order [11]. This O'/O'' transition is clearly indicated in the resistivity results [13] but also in the susceptibility data (see Fig. 1). The structural OO' phase transitions which appear close to room temperature for $0.1 \leq x \leq 0.125$ can be determined from the inverse susceptibility *vs.* temperature (not shown here).

All the observed anomalies are indicated in the $x-T$ phase diagram which is shown in Fig. 4. At low concentrations ($x < 0.1$) we find an insulating orthorhombic phase O' which reveals canted antiferromagnetism at low temperatures. In a narrow temperature range at elevated temperatures these phase extends up to $x = 0.15$. Again the PM insulator is followed by an insulating CA phase. The "metallic behavior" ($\frac{d\rho}{dT} < 0$) in this regime obviously results from the freezing-out of spin-disorder. For $0.1 \leq x \leq 0.15$ the ground state is a FM insulator with a pseudocubic O phase and charge (Mn³⁺/Mn⁴⁺) order, further denoted as O'' [15]. At the O'O'' transition, which is followed by the FM transition, the resistivity steeply increases. For $x > 0.17$ the ground state is a FM metal revealing an O structure for $x < 0.2$ and a rhombohedral structure for $x > 0.2$. The phase diagram around strontium concentrations 0.15 is unclear. Here the different magnetic and structural phase boundaries meet and phase separation may be a natural explanation of the experimental results.

Here we recall the most important result of this study. Close to $x = 0.125$ we provide experimental evidence for the sequence: O/PM \rightarrow O'/PM \rightarrow O'/CA \rightarrow O''/CA \rightarrow O''/FM. From our magnetoresistance measurements, which will be published in a forthcoming paper we found a positive MR in the O''/CA phase, while large and enhanced negative MR effects appear close to the O'/PM to O'/CA phase boundary. A positive MR has also been reported by Senis *et al.* [20].

A simple explanation of the observed structural and magnetic phase diagram can be given by taking SE interactions into account. For $x = 0$, in the pure compound the MnO₆ octahedra reveal a cooperative rotation about the orthorhombic b-axis. This rotation produces anisotropic Mn-O-Mn bonds, which in turn give FM exchange interactions within the a-b planes and AFM interactions along the c-axis and yield the A-type AFM structure of LaMnO₃ [12,21]. In the non-JT distorted O phase the SE is isotropic, yielding three-dimensional FM interactions between Mn³⁺ and Mn³⁺ as well as Mn³⁺ and Mn⁴⁺. Hence the low-temperature structures of O and O'' which both are pseudocubic, reveal FM order. Within the O' phase the decrease of the canting angle may well be determined by DE interactions and DE certainly plays an important role for $x > 0.175$, but the ferromagnetism of the O'' phase definitely is determined by structural properties, namely the isotropic superexchange interactions of the pseudocubic perovskite structure.

This work has in part be supported by the BMBF under the contract number 13N6917.

-
- [1] G. H. Jonker and J. H. van Santen, *Physica* **16**, 337 (1950).
- [2] E. O. Wollan and V. C. Koehler, *Phys. Rev.* **100**, 545 (1955).
- [3] P. G. de Gennes, *Phys. Rev.* **118**, 141 (1960).
- [4] C. Zener, *Phys. Rev.* **82**, 403 (1951).
- [5] K. Chahara, T. Ohno, M. Kasai and Y. Kozono, *Appl. Phys. Lett.* **63**, 1990 (1993); R. von Helmot, J. Wecker, B. Holzapfel, L. Schulz and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993); S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh and L. H. Chen, *Science* **264**, 413 (1994).
- [6] N. Furukawa, *J. Phys. Soc. Jpn.* **63**, 3214 (1994).
- [7] A. J. Millis, P. B. Littlewood and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995); I. Solovyev, N. Hamada and K. Terakura, *Phys. Rev. Lett.* **76**, 4825 (1996).
- [8] A. K. Bogush, V. I. Pavlov and L. V. Balyko, *Cryst. Res. Technol.* **18**, 589 (1983).
- [9] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido and Y. Tokura, *Phys. Rev. B* **51**, 14103 (1995).
- [10] H. Kawano, R. Kajimoto, M. Kubota and H. Yoshizawa, *Phys. Rev. B* **53**, 2202 (1996); H. Kawano, R. Kajimoto, M. Kubota and H. Yoshizawa, *Phys. Rev. B* **53**, R14709 (1996).
- [11] Y. Yamada, O. Hino, S. Nohdo and R. Kanao, *Phys. Rev. Lett.* **77**, 904 (1996).
- [12] J.-S. Zhou, J. B. Goodenough, A. Asamitsu and Y. Tokura, *Phys. Rev. Lett.* **79**, 3234 (1997).
- [13] A. A. Mukhin, V. Y. Ivanov, V. D. Travkin, S. P. Lebedev, A. Pimenov, A. Loidl and M. Balbashov, *JETP Letters* **69**, 356 (1998).
- [14] D. N. Argyriou, J. F. Mitchell, C. D. Potter, D. G. Hinks, J. D. Jorgensen and S. D. Bader, *Phys. Rev. Lett.* **76**, 3826 (1996).
- [15] L. Pinsard, J. Rodríguez-Carvajal, A. H. Mouden, A. Anane, A. Revcolevschi and C. Dupas, *Physica B* **234-236**, 856 (1997); L. Pinsard, J. Rodríguez-Carvajal and A. Revcolevschi, *J. Alloys and Compounds* **262-263**, 152 (1997).
- [16] A. Asamitsu, Y. Moritomo, R. Kumai, Y. Tomioka and Y. Tokura, *Phys. Rev. B* **54**, 1716 (1996).
- [17] Y. Murakami, J. P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, Y. Tokura, K. Hirota and Y. Endoh, *Phys. Rev. Lett.* **81**, 582 (1998).
- [18] S. Yunoki, J. Hu, A. L. Malvezzi, A. Moreo, N. Furukawa and E. Dagotto, *Phys. Rev. Lett.* **80**, 845 (1998).
- [19] G. Allodi, R. De Renzi, G. Guidi, F. Licci and M. W. Pieper, *Phys. Rev. B* **56**, 6036 (1997).
- [20] R. Senis, V. Laukhin, B. Martínez, J. Fontcuberta, and X. Obradors, *Phys. Rev. B* **57**, 14680 (1998).
- [21] J. Töpfer and J. B. Goodenough, *J. Solid State Chem.* **130**, 117 (1997).

FIGURE CAPTIONS:

Fig. 1: AC susceptibility *vs.* temperature in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for concentrations $x = 0.1, 0.125$ and 0.15 . The inset shows the susceptibilities for $x = 0, 0.05$ and 0.075 on a semi-logarithmic scale.

Fig. 2: Magnetization *vs.* magnetic field for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for concentrations $x = 0, 0.05, 0.075, 0.1$ and 0.2 at 10 K. The inset a) shows an enlarged view of the FM hysteresis loops at small fields. Inset b) shows the spontaneous magnetization M_S as a function of x .

Fig. 3: Magnetization *vs.* field as observed in $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ at different temperatures between room temperature and 10 K.

Fig. 4: $x - T$ phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The structural (O, O', O'', R), magnetic (PM, CA, FM) and electronic (M, I) phases are indicated. Open symbols (dashed lines) denote structural phase boundaries, solid symbols (full lines) denote magnetic phase boundaries.







